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Poly(*p*-phenylene) Derivatives New High Performance Nonlinear Optical Polymers

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NLO polymers (NLOPs) based on the poly(*p*-phenylene) (PPP) backbone were prepared in the study. The thermal stability for the new materials is presented. The polymer displayed a T_g of 220 deg C. The TGA scan of the material indicated reasonable thermal stability to 300 deg C. A thin film of the material was supported on a glass slide and heated at 200 deg C and monitored by UV-vis spectroscopy. These experiments indicated less than 10% loss of the absorption band due to the NLO-phore (*i.e.* chromophore) over a period of 24 h.

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Poly(*p*-phenylene) Derivatives: New High Performance Nonlinear Optical Polymers

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Introduction

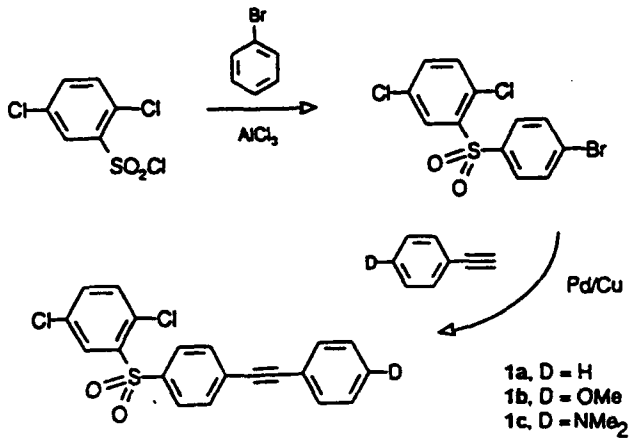
Nonlinear optical (NLO) materials research has become a very mature and sophisticated area of polymer chemistry.[1] The design criteria for NLO active molecules which have $\chi^{(2)}$ activity is well established.[2] Many of the original criterion applied to $\chi^{(2)}$ NLO materials have changed with the recent discovery of light emitting polymer based devices.[3] One current area of focus in NLO materials is the development of photonic devices.[4] NLO polymers (NLOP) have shown great promise for device applications. NLOP's have large optical nonlinearities, super fast response time (GHz), and often exhibit high damage thresholds (>10^9 MW cm^{-2}). It appears that NLOP's can match the challenges found in this rapidly developing area of advanced technology.[5] The thermal stability of NLOP materials is of primary concern and is an issue currently of interest.

In this paper, we will present results from our synthetic studies targeted at preparing high-performance NLO polymers based on poly(*p*-phenylene).

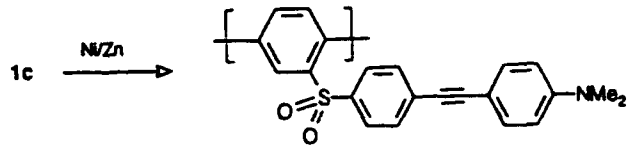
Results and Discussion

We have prepared a series of *p*-dichlorophenylene monomers containing tolane based NLO-phores (Scheme I). These NLO-phores were selected on the basis of their fairly large hyperpolarizability and reasonably good thermal stability.

Scheme I



The monomers were polymerized using the Ni/Zn mediated homocoupling[6] to afford poly(*p*-phenylenes) in moderate yield with a range of molecular weights. Polymer **2c** was produced in the highest yield and molecular weight (M_n = ~8,000).



2c

DSC analysis of polymer **2c** shows a strong T_g at 220 °C. The polymer is soluble in common organic solvents and solutions of **2c** can be spin-cast to produce films of high optical quality. Thermal stability of **2c** is excellent to 300 °C and above that temperature we see decomposition of the NLO-phore side-chain. Optical studies are underway (Prof. H. Lackritz and Kirk Wilson, Purdue University) and will be briefly discussed in the presentation.

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